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(54) BATTERY INCORPORATING ORGANIC/INORGANIC COMPOSITE POLYMER SOLID ELECTROLYTE

(57)Abstract:
PROBLEM TO BE SOLVED: To provide a battery incorporating an organic/inorganic composite polymer solid electrolyte having high ion conductivity at a relatively low temperature, great physical strength in a thin membrane form and superior heat resistance.
SOLUTION: The lithium secondary battery incorporates an organic/inorganic composite polymer solid electrolyte membrane containing containing (1) an organic polymer compound having at least one type of main chains containing oxygen atoms, (2) at least one type of inorganic oxide and (3) lithium electrolyte salt. If the average particles size of (2) the inorganic oxide is 100 nm or smaller and the sum of (1) the polymer compound and (2) the inorganic oxide is 100%, the lithium secondary battery contains (2) the inorganic oxide of 10-30 wt.% or so and has the solid

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CLAIMS

[Claim(s)]
[Claim 1](1) An organic polymer compound which contains an oxygen atom in a kind of main chain at least, (2) It is the lithium secondary battery which incorporated at least the inorganic matter / organic compound Polymer Division solid-electrolyte membrane containing a kind of inorganic oxide and (3) lithium-electrolyte salt, - A lithium secondary battery whose thickness of - solid-electrolyte membrane mean particle diameter of (2) inorganic oxides is 100 nm or less, (2) inorganic oxides are included at about 10 to 30% of the weight of a rate, and is 40 micrometers or less when the sum of - (1) high molecular compound and (2) inorganic oxides is made into 100%.
[Claim 2](1) The lithium secondary battery according to claim 1 whose high molecular compounds are with a molecular weights of 100,000 or more polyethylene oxide and/or its derivative.
[Claim 3](2) The lithium secondary battery according to claim 1 or 2 which is an oxide of an element chosen from a group which an inorganic oxide becomes from silicon, titanium, and a zirconium.
[Claim 4](2) The lithium secondary battery according to claim 3 whose inorganic oxide is an oxide of silicon.
[Claim 5]A lithium electrolyte salt (3) $LiN(CF_3SO_2)_2$, The lithium secondary battery according to any one of claims 1 to 4 which is at least one sort chosen from a group which consists of $LiCF_3SO_3$, $LiPF_6$, $LiBF_4$, and $LiClO_4$.
[Claim 6](3) The lithium secondary battery according to claim 5 whose lithium electrolyte salt is $LiN(CF_3SO_2)_2$.
[Claim 7]The lithium secondary battery according to any one of claims 1 to 6 which uses as an anode a compound anode which consists of a solid polymer electrolyte and an oxide using a lithium metal or its alloy as a negative electrode of a cell.
[Claim 8]The lithium secondary battery according to claim 7 whose oxide in a compound anode is Li_xMnO_2 (x= 0.1-0.5).
[Claim 9]The lithium secondary battery according to claim 7 or 8 whose solid polymer electrolytes

in a compound anode are with a molecular weight of 3000 or less polyethylene oxide and/or its derivative.

[Claim 10]The lithium secondary battery according to claim 9 in which polyethylene oxide and/or its derivative are polyethylene-glycol wood ether.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention]This invention relates to the outstanding ion conductivity and the solid polymer electrolyte which has intensity which can be used for a lithium secondary battery etc.
[0002]
[Description of the Prior Art]As everyone knows, the rechargeable battery used for a portable personal computer, a video camera, etc. in recent years is high energy density, and a long time of the charge-and-discharge cycle life is called for. simultaneous -- the miniaturization of a cell, a weight saving, and slimming down (sheet-izing) -- expansion of shape flexibility, etc. are demanded further strongly.
[0003]As a rechargeable battery from the former, although a lead storage battery, a nickel-cadmium battery, a nickel hydoride battery, etc. are used widely, a rechargeable lithium-ion battery is further put in practical use as a rechargeable battery of high energy density, and the Schar is lengthened quickly in recent years.
[0004]Although it is common to an electrolyte that a fluid is used as for each of these conventional rechargeable batteries and the organic solvent of a non-drainage system, etc. have been used for solution, such as inorganic acid and alkali, and a lithium ion battery, These are dangerous fluids when it reveals, and the consideration for the safety had become the big restrictions on a cell design.
[0005]On the other hand, in the case of a rechargeable lithium-ion battery, although the carbon material which can intercalate a lithium ion is generally used for the negative electrode, originally, it is more advantageous, direction using [energy density] a lithium metal or its alloy. However, when the electrolyte using lithium and a lithium metal as a negative electrode is a solution type lithium cell, a needlelike lithium metal (dendrite) deposits on a negative electrode with a repetition of charge and discharge at the time of use, and there is a problem that this gives a damage to a separator and causes the short circuit of a cell.
[0006]Then, it has dealt with the trial which makes an electrolyte a solid state as a means to avoid

this fault, and prevents liquid leakage early. It is supposed that there is an effect which controls generation of the dendrite at the time of using a lithium metal etc. for said negative electrode solidifying.

[0007]From these things, development of the solid electrolyte which was excellent in the performance which has high ionic conductivity and high intensity was desired, and energetic examination has been advanced. Although the mainstream is an oxygen atom content organic polymer compound of a polyethylene oxide system, the ionic conductivity in the room temperature is low as compared with a liquid electrolyte, and 10^{-4} - a 10^{-5}S/cm grade are limits.

[0008]Although development of the electrolyte of the gel type which made the liquid component (solvent) contain is also simultaneously advanced to the high molecular compound and it depends for the ionic conductivity also on the solvent to contain, in the case of Polymer Division which can be contained so much, there is also a report of the level in which the utilization more than 10^{-3}S/cm is possible. However, in the case of these gel electrolytes, when the strength reduction by being impregnated of a solvent and welding pressure act, there are problems, such as extraction of a solvent.

[0009]The method which applies a solid electrolyte to the base fabric which has the intensity of the fine porous membrane of a high molecular compound, a nonwoven fabric, textiles, etc. and with which it is impregnated as a method of improving the intensity fault of this gel electrolyte is proposed variously. In the case of these proposals, since the base fabric to be used is mainly a polyolefin system, there is a limit also in a heatproof and an intensity target, and there is technical difficulty also in being impregnated of a high molecular compound, and spreading.

[0010]The method of using for a base fabric the aramid fiber which are all the aroma group polyamide as a method which improved the aforementioned fault is proposed by JP,H11-339555,A. However, as for the thickness of the electrolyte membrane obtained, by a we method, 40-50 micrometers is considered to be a limit.

[0011]

[Problem(s) to be Solved by the Invention]Like ****, as for the thickness to which the solid electrolyte proposed until now can present practical use with the ionic conductivity in a room temperature from 10^{-4}S/cm and its intensity, 50 micrometers is considered to be a limit, respectively. Therefore, the purpose of this invention is to provide the lithium secondary battery incorporating a solid electrolyte applicable to a cell by having desired ionic conductivity, having desired intensity, without using a base material, a base fabric, etc., and being able to make thickness thin by that cause.

[0012]

[Means for Solving the Problem]The purpose of this invention is to develop a solid polymer electrolyte which satisfies fundamentally stability at the time of applying to high ionic conductivity, a high mechanical strength, and a cell, and to apply it to a metallic lithium battery of high energy density as a thin film of 40 micrometers or less with small internal resistance suitable for a cell. This invention persons thought that there was a limit in ionic conductivity of a pure solid polymer

electrolyte, and inquired by mixing an inorganic oxide.

[0013]Although history of research of a composite high polymer electrolyte (composite polymer electrolyte) can be traced back ten years or more ago, Although there are "character of polymer and crystalline ionic conductor mixture""PHILOSOPHICAL MAGAZINE"B, such as B.SCROSATI, 1989, Vol.59, and No.1,161-168 as a typical example, also after that, research energetic till the present is continued. however, SHISUTEMA as a cell, especially a lithium cell -- there are few application studies [tic] and a report of a cell combined with a lithium metal negative electrode as a thin film of 50 micrometers or less is not found.

[0014]A factor required in order to complete a highly efficient polymer battery is that ionic conductivity of a solid polymer electrolyte is high first. Although there are methods, such as adding branching, composition of an organic polymer compound containing oxygen which has the structure of cross linkage, addition of a plasticizer, and an inorganic compound as a typical means which raises ionic conductivity, and considering it as inorganic matter/organic complex, Methods other than addition of a plasticizer are un-crystallizing Polymer Division and raising the mobility of ion. This invention persons tackle development of inorganic matter / organic compound solid polymer electrolyte excellent in ion conductivity, and came to complete this invention.

[0015]To namely, polyethylene oxide (PEO) of base polymer, this invention persons, and/or its derivative. Among a specific amount, i.e., the total quantity of polymer and pulverized coal, mix ten to 30% of the weight, and pulverized coal of oxides, such as silicon below fixed particle diameter, and titanium, as a lithium electrolyte salt, For example, filmy inorganic matter / organic composite high polymer electrolyte added and obtained so that it might be set to 1-30 by an EO/Li mole ratio in Polymer Division, such as polyethylene oxide, $LiN(CF_3SO_2)_2$ (it may abbreviate to LiTFSI hereafter) with high ionic conductivity. It found out having the outstanding mechanical strength. Namely, this invention persons can adjust average thickness of an electrolyte membrane enough at 40 micrometers, The ionic conductivity succeeded in creation of all the solid lithium-polymer batteries which used 3V system manganic acid ghost for metal lithium or its alloy, and an anode at a negative electrode using a solid polymer electrolyte of this thin film that is 2.2 - $5.5x10^{-4}$S/cm in 60 **.

[0016]It became clear by this invention persons' further research that raising ion conductivity as organicity/inorganic composite has an advantage big in addition to this. Namely, although it was known as a composite material that a mechanical strength of polymer will go up by complex-izing, as for application to a thin film of micron order, examination get wet, complicated conditions, such as a dispersion state, and sufficient with Polymer Division in particle diameter and an interface was not made.

[0017]This invention persons were carrying out uniform dispersion of the inorganic oxide which has the particle diameter of a still more specific range, and their internal resistance was small and they found out suitable for a lithium secondary battery being a thin film, and that a 10-40-micrometer thin film was specifically producible with sufficient reproducibility.

[0018]This invention provides the following inventions.

[0019]Paragraph 1. (1) An organic polymer compound which contains an oxygen atom in a kind of main chain at least, (2) It is the lithium secondary battery which incorporated at least the inorganic matter / organic compound Polymer Division solid-electrolyte membrane containing a kind of inorganic oxide and (3) lithium-electrolyte salt, - A lithium secondary battery whose thickness of - solid-electrolyte membrane mean particle diameter of (2) inorganic oxides is 100 nm or less, (2) inorganic oxides are included at about 10 to 30% of the weight of a rate, and is 40 micrometers or less when the sum of - (1) high molecular compound and (2) inorganic oxides is made into 100%.
[0020]Paragraph 2. Lithium secondary battery given in the paragraph 1 whose (1) high molecular compounds are with a molecular weights of 100,000 or more polyethylene oxide and/or its derivative.
[0021]Paragraph 3. Lithium secondary battery given in the paragraph 1 or 2 which is the oxides of an element chosen from a group which (2) inorganic oxides become from silicon, titanium, and a zirconium.
[0022]Paragraph 4. Lithium secondary battery given in the paragraph 3 whose (2) inorganic oxides are oxides of silicon.
[0023]Paragraph 5. (3) lithium-electrolyte salt $LiN(CF_3SO_2)_2$, A lithium secondary battery given in either of the paragraphs 1-4 which are at least one sort chosen from a group which consists of $LiCF_3SO_3$, $LiPF_6$, $LiBF_4$, and $LiClO_4$.
[0024]Paragraph 6. Lithium secondary battery given in the paragraph 5 whose (3) lithium-electrolyte salt is $LiN(CF_3SO_2)_2$.
[0025]Paragraph 7. Lithium secondary battery given in either of the paragraphs 1-6 which uses as an anode a compound anode which consists of a solid polymer electrolyte and an oxide using a lithium metal or its alloy as a negative electrode of a cell.
[0026]Paragraph 8. Lithium secondary battery given in the paragraph 7 whose oxide in a compound anode is Li_xMnO_2 (x= 0.1-0.5).
[0027]Paragraph 9. The paragraph 7 whose solid polymer electrolytes in a compound anode are with a molecular weight of 3000 or less polyethylene oxide and/or its derivative, or lithium secondary battery given in 8.
[0028]Paragraph 10. Lithium secondary battery given in the paragraph 9 in which polyethylene oxide and/or its derivative are polyethylene-glycol wood ether.
[0029]
[Embodiment of the Invention]It is hereafter attached to the inorganic matter / organic compound solid polymer electrolyte of this invention, and the cell incorporating it, and explains. The solid electrolyte of this invention receives oxygen atom content organic polymer compounds, such as polyethylene oxide and/or its derivative, Particle diameter adds inorganic oxides, such as silicon of 100 nm or less, titanium, and zirconia, ten to 30% of the weight among the total quantity of this high molecular compound and an inorganic oxide, It has the outstanding characteristic which the ionic conductivity, a mechanical strength, heat resistance, etc. are raised, and is replaced with the

organic electrolysis liquid of 40 micrometers or less of a lithium cell which can be made filmy.

[0030]In organic polymer compound (oxygen atom content organic polymer compound) this invention containing an oxygen atom, a polyether system compound is mentioned to a main chain as an oxygen atom content organic polymer compound, for example. As a polyether system compound, polyethylene oxide, polypropylene oxide, polyoxymethylenes, or these derivatives can be illustrated.

[0031]Especially if the molecular weight of these high molecular compounds is a size which can be used as a solid electrolyte, it will not be restricted, but 100,000 or more molecular weights are about 1 million to 4 million thing more preferably 5 million or less [500,000 or more].

[0032]being able to manufacture these high molecular compounds by a publicly known method, and setting them to this invention -- a kind -- or two or more sorts may use it, mixing. The mixing ratio in particular is not limited, either.

[0033]As an inorganic oxide used by inorganic oxide this invention, Especially if it is an oxide of a single element and its mixture, an oxide of two or more sorts of elements, and its mixture, it will not be limited, but silicon (Si), titanium (Ti), a zirconium (Zr), aluminum (aluminum), calcium (Ca), magnesium (Mg), etc. can be illustrated, for example. Preferably, it is an oxide of the metal chosen from silicon, titanium, and a zirconium. More specifically, SiO_2, TiO_2, and ZrO_2 can be illustrated. It is SiO_2 at the more desirable low-cost point which is easy to manufacture at the oxide of silicon, and a concrete target.

[0034]The shape of a grain can be illustrated as shape of these inorganic compounds. As the size, 100 nm or less of mean particle diameter [about 50 nm or less of] at the time of planning by the following measuring methods is specifically about 1-20 nm preferably. If larger than a mentioned range, conductivity will fall, and if production of a thin film is difficult and smaller than a mentioned range, the problem to which intensity falls will arise.

[0035]A measuring method of particle diameter: Mean-particle-diameter D_{50} was measured using the size distribution measuring device.

[0036]being able to manufacture these inorganic oxides by a publicly known method, and setting them to this invention -- a kind -- or two or more sorts may use it, mixing. The mixing ratio in particular is not limited, either.

[0037]The mixing ratio of an inorganic oxide is preferably added ten to 20% of the weight ten to 30% of the weight among the mixed amount (100 % of the weight) of an oxygen atom content organic polymer compound and an inorganic oxide. If conductivity falls and there is a problem to which film production becomes difficult, when it blends more mostly than a mentioned range, and it blends few, the addition effect will not be seen, but the problem whose ionic conductivity and intensity cannot improve arises.

[0038]About the obtained thin film, ionic conductivity was measured, it included in the negative electrode as an electrolyte of the cell which uses a lithium manganic acid ghost for metal lithium and an anode, and the quality assessment was carried out. Although the needlelike lithium metal (dendrite) deposited in the surface of metal and the organic electrolysis liquid cell which generally

uses metal lithium for a negative electrode as described above caused the short circuit of the cell to it, when the solid was used for the electrolyte, since the reaction of an electrolyte and lithium was comparatively loose, it was presupposed that this phenomenon is controlled.

[0039]In this invention persons' trial result, when the cell was constructed by lithium / solid electrolyte / lithium manganic acid ghost by having used as the solid electrolyte the polymer thin film which does not add an inorganic oxide and the charge-and-discharge test was done, it turned out that a cell short-circuits comparatively for a short time. It is thought that this phenomenon is the result of the generated dendrite destroying a separator film. Therefore, since it turned out that generation of a dendrite can be used as an alternative characteristic to express, time until it connects too hastily by the charge-and-discharge test of a cell was used for the evaluation which shows the mechanical strength of the following various inorganic matter / organic compound solid polymer electrolytes.

[0040]This fact shows that the mechanical physical properties (strength) of the thin film of a solid polymer electrolyte are the important requirements as a solid electrolyte which was excellent with peculiar ionic conductivity. The ion conductivity of Polymer Division of a polyethylene oxide system shall have depended on the segmental motion of the polar group in the Polymer Division chain. Therefore, in order to make segmental motion easy, it is necessary to control crystallization of Polymer Division, and an inorganic oxide is added in this invention.

[0041]This invention persons found out the phenomenon of being hard to be influenced by the dendrite generation at the time of considering it as the cell which uses metal lithium for a negative electrode with improvement in ionic conductivity, when the inorganic oxide specific to an organic polymer compound as mentioned above etc. were added. Addition of the specific inorganic oxide raised the mechanical strength of the Polymer Division solid-electrolyte membrane, and this thinks that the film break life which depends on dendrite generation as a result is lengthened.

[0042]The solid electrolyte of a lithium electrolyte Shiomoto invention contains a lithium electrolyte salt further. As this lithium electrolyte salt, alkali metal salt, such as $LiN(CF_3SO_2)_2$, $LiCF_3SO_3$, $LiPF_6$, $LiBF_4$, and $LiClO_4$, etc. are mentioned. Preferably, it is $LiN(CF_3SO_2)_2$. these electrolyte salt is publicly known compounds -- a kind -- or two or more sorts may be mixed, it may use, and the mixing ratio is not limited.

[0043]the blending ratio of a lithium metal salt to an oxygen atom content organic polymer compound -- the ethylene oxide (EO)/Li mole ratio in this high molecular compound -- 1-30 -- it mixes so that it may become a rate of 5-25 preferably. this atomic ratio -- a mentioned range -- it is large (that is, there are few blending ratios of a lithium metal salt) -- ionic conductivity falls -- this atomic ratio -- a mentioned range -- it is small (that is, there are many blending ratios of a lithium metal salt) -- the problem which becomes low also produces conductivity.

[0044]The solid electrolyte of solid electrolyte this invention can be manufactured, for example in accordance with the following methods. That is, the oxygen atom content organic polymer compound and inorganic oxide of the above-mentioned description are mixed in a mentioned range. As for an inorganic compound, it is preferred to carry out heat treatment etc. a priori in order

to remove moisture.

[0045]Especially as a mixing method, without being restricted, especially if it is a mixed (for example, a wet type, dry-type mixing) method usually used, it will not be restricted, but it is preferred to, use a mill (for example, planet type ball mill) etc. for example. As for mixing, it is preferred to carry out making it rotate. Number of rotations in particular is not limited.

[0046]When mixing time uses the planet type ball mill of the number of rotations of 100 rpm., for example, about 2 to 24 hours and a mixed temperature are room temperature grades, but mixing time and a mixed temperature in particular are not limited, either, but can be performed in the range by which normal use is carried out. By the above-mentioned mixing, an inorganic oxide carries out uniform dispersion into this high molecular compound.

[0047]At an above-mentioned rate, a lithium electrolyte is added to the obtained mixture and it mixes into it. A mixing method in particular is not limited but handicraft, machinery mixing, etc. are mentioned. In order to avoid moisture, it is preferred to carry out in dry room.

[0048]The obtained mixture is fabricated filmy so that it can be used with the solid electrolyte separator of a totally-solid battery. Although not restricted especially as a forming process, it inserts into a mold releasing film and a film-like solid electrolyte is obtained by carrying out a hotpress about 1 to 30 minutes under application of pressure ($1x10^2$ - $5x10^3 N/cm^2$) at about 60-100 **, for example.

[0049]Or it may manufacture also with solvent method (how to make a solvent distill off and produce [melts the mixture obtained in solvents, such as acetonitrile and a tetrahydrofuran, and slushes into a mold releasing film, and] a film by heating).

[0050]It is good to obtain desired ionic conductivity and mechanical strength also as 40 micrometers or less, and to be preferably referred to as about 15-30 micrometers as thickness of this film.

[0051]The solid-electrolyte membrane obtained by the described method can take a high value called [on 60 ** and] $2.5x10^{-4}$ - a $5.5x10^{-4}$ S/cm grade in ionic conductivity.

[0052]Above-mentioned inorganic matter / organic compound solid polymer electrolyte are used for the lithium secondary battery of cell this invention of this invention. That is, the battery element of publicly known lithium secondary batteries (a coin type, a button type, cylindrical, a square shape, a laminated type, etc.) is employable as it is except using the solid electrolyte of this invention as an electrolyte.

[0053]Therefore, as an anode, oxides, such as Li_xCoO_2, Li_xNiO_2, $Li_xMn_2O_4$, VO_x, CrO_x, and a manganic acid ghost, can be illustrated as an electrode active material, for example. Preferably, it is $Li_xMn_2O_4$ (x= 0.1-0.5). What is necessary is to usually use the publicly known above-mentioned electrode active material about creation of an anode, and also just to carry out in accordance with the manufacturing method of a publicly known electrode.

[0054]In this invention, it is preferred to use the compound anode which consists of a solid polymer electrolyte and the above-mentioned oxide. As ** and a solid polymer electrolyte, with a molecular weight of 3000 or less polyethylene oxide and/or its derivatives (for example, polyethylene-glycol

wood ether, polyethylene-glycol diethylether, polyethylene-glycol diaryl ether, etc.) can be illustrated, for example. Preferably, polyethylene-glycol wood ether is mentioned.

[0055]Although it is possible to use the negative electrode containing negative electrode active material usually publicly known also as a negative electrode, metal lithium and a lithium alloy can be used, for example. Preferably, it is metal lithium. What is necessary is just to follow the method that creation of a negative electrode is also publicly known.

[0056]When carrying out the charge and discharge of the cell of this invention by current density 0.2 mA/cm^2 in 60 ** as battery capacity, the service capacity after 100 cycles has not less than 75% of performance of initial service capacity.

[0057]What is used for a publicly known rechargeable battery as other components can be used as a component, and there is no restriction in particular.

[0058]What is necessary is just to assemble the cell of this invention in accordance with a publicly known method using these battery elements. In this case, the shape of a coin type, a button type, cylindrical, a square shape, a laminated type, etc. and size can be adopted suitably, for example, without being restricted also especially about cell shape.

[0059]

[Effect of the Invention]According to this invention, the inorganic matter / organic compound Polymer Division solid-electrolyte membrane of 10 micrometers - the 40-micrometer range have been produced with sufficient reproducibility by carrying out uniform dispersion of the inorganic oxide of the particle diameter of a nano level with a specific ratio. The conductivity improved more than twice in 60 **, and further, since a mechanical strength went up notably, the effect that generation of a dendrite was controlled by the metal lithium surface has been demonstrated.

[0060]

[Example]Although working example and a comparative example are shown and the place by which it is characterized [of this invention] is clarified further hereafter, this invention is not necessarily limited to these working example.

[0061]Working example 1-4 and the comparative example 1 - 4 inorganic matter / organic compound Polymer Division solid-electrolyte membrane as ******-SUPORIMA of the incorporated cell Polyethylene oxide (PEO) (made by ADORITCHI) of the molecular weight 4 million, Weighing of the silicon oxide (SiO_2) (made by Nippon Sheet Glass Co., Ltd.) with a mean particle diameter of 10 nm was carried out as an inorganic oxide, and it mixed at the number of rotations of 100 rpm with the room temperature with the weight percentage shown in Table 1 for 12 hours or more using the planet type ball mill. the obtained mixture -- the inside of dry room -- the rate of [EO]/[Li]=20 -- as a lithium electrolyte salt -- a lithiumimide salt (LiTFSI) -- in addition, it mixed uniformly in the mortar. A constant rate of this mixture was inserted into the 50-micrometer-thick mold releasing film made from polyester, the film was produced with the hotpress for 10 minutes under the pressure of temperature, $2x10^2$ - $1x10^3 N/cm^2$ of 75 **, and inorganic matter / organic compound Polymer Division solid-electrolyte membrane 40-micrometer were obtained.

[0062]Polyethylene-glycol wood ether +LiTFSI=65/5/30 of <compound anode> $Li_{0.33}MnO_2$ /

Ketchen black (KB) / molecular weight 2000 (with polyethylene-glycol wood ether and LiTFSI.) It mixed in the mortar by the weight ratio of 20 by the EO/Li mole ratio, and ********** was applied on the aluminium foil charge collector, and created the compound anode of the holding amount of 5 mg / cm^2 of manganic acid lithium.

[0063]An assembly procedure of the cell for conductivity measurement, the cell for a cell test, and the cell for cell short-circuit-duration measurement and a test method for the same are explained below to <an assembly and test method of a cell>.

[0064]On both sides of the solid polyelectrolyte membrane for measurement (area 1.2cm^2 and 40 micrometers in thickness), the cell was assembled in two stainless steel disks (area 2cm^2) of cell 0.8 cmxphi for conductivity measurement. Temperature was changed for this cell in the thermostat, resistance was measured with the impedance measuring equipment by EG&G INSTRUMENT, and it asked for the conductivity in each temperature.

[0065]The solid-electrolyte membrane was pinched between the anode (area 1.2cm^2) created by the method of the cell above for a cell test, and the metal lithium negative electrode (area 1.0cm^2 and 0.5 mm in thickness), and a coin type cell or its lamination encapsulated type cell was assembled. The charge-and-discharge test was carried out using the Measuring instrument Center charge and discharge system using this cell between temperature [of 60 **], and current density 0.2mA/cm^2, and the voltage ranges 2.0V-3.5V.

[0066]On both sides of the cell height molecular-solid electrolyte membrane for cell short-circuit-duration measurement, the cell was assembled with two metal lithium (area 1.0cm^2 and 0.5 mm in thickness) boards. Time to connect too hastily by performing charge and discharge in 60 ** using this cell between current density/cm[of 0.5 mA] ^{2}, voltage range 1.0V --1.0V shall be measured, and it shall originate in a dendrite.

[0067]The result of the above-mentioned examination is shown in Table 1.

[0068]

[Table 1]

		固体電解質中の配合割合(重量%)				膜厚(μm)	膜特性		"電池特性(%)(60℃)
		(1) PEO	(2) SiO_2粒径(nm) 10	90	200		導電率(×10^{-4}S/cm)	'D時間(時間)	
実施例	1	90	10	—	—	40	4.51	12.7	85
	2	80	20	—	—		5.42	14.2	87
	3	80	—	20	—		2.76	11.8	80
	4	70	30	—	—		3.05	12.5	78
比較例	1	100	—	—	—		1.99	1.5	40
	2	95	5	—	—		1.99	3.0	45
	3	80	—	—	20		2.13	2.3	45
	4	60	40	—	—		0.61	1.4	40

＊D時間：60℃において電流密度0．5mA／cm^2で充放電するとき、デンドライトが生成するため短絡する時間である。

＊＊電池性能：60℃において電流密度0．2mA／cm^2で充放電するとき、100サイクルの放電容量（初期容量を100％として換算）

[0069]Except having been referred to as the thickness of working example 5-7 and comparative

example 5 solid-electrolyte membrane, and 15-50 micrometers, the cell and the cell were assembled like working example 2, and each characteristic was evaluated.

[0070]A result is shown in Table 2.

[0071]

[Table 2]

		固体電解質中の配合割合（重量%）		膜厚（μm）	膜特性		**電池特性（%）（60℃）
		(1) PEO	(2) SiO_2粒径 10 (nm)		導電率（×10^{-4}S/cm）	*D時間（時間）	
実施例	5	80	20	15	5．43	11.2	94
	6			20	5．42	13.4	90
	7			30	5．42	13.8	88
	2			40	5．42	14.2	87
比較例5				50	5．39	15.0	62

＊D時間：６０℃において電流密度０．５ｍＡ／ｃｍ²で充放電するとき、デンドライトが生成するため短絡する時間である。

＊＊電池性能：６０℃において電流密度０．２ｍＡ／ｃｍ²で充放電するとき、１００サイクルの放電容量（初期容量を１００％として換算）

[0072]It carried out like working example 1 except using titanium oxide and oxidation zirconia as six to working example 8-17 and comparative example 11 inorganic oxide. A result is shown below.

[0073]

[Table 3]

		固体電解質中の配合割合（重量%）				膜厚（μm）	膜特性		**電池特性（%）（60℃）
		(1) PEO	(2) TiO_2粒径 (nm)				導電率（×10^{-4}S/cm）	*D時間（hr.）	
			10	90	200				
実施例	8	90	10	—	—	40	3.36	12.5	83
	9	80	20	—	—	40	4.32	13.8	84
	10	80	20	—	—	20	4.47	13.1	87
	11	80	—	20	—	40	2.16	11.7	77
	12	70	30	—	—	20	2.93	11.9	81
比較例	6	95	5	—	—	40	1.95	2.4	40
	7	60	40	—	—	40	0.58	1.3	39
	8	80	—	—	20	40	2.03	1.6	42

＊D時間：６０℃において電流密度０．５ｍＡ／ｃｍ²で充放電するとき、デンドライトが生成するため短絡する時間である。

＊＊電池性能：６０℃において電流密度０．２ｍＡ／ｃｍ²で充放電するとき、１００サイクルの放電容量（初期容量を１００％として換算）

[0074]

[Table 4]

		固体電解質中の配合割合（重量%）				膜厚（μm）	膜特性		**電池特性（*）（60℃）
		(1) PEO	ZrO_2粒径（nm）				導電率（$\times 10^{-4}$S/cm）	*D時間（hr.）	
			10	90	200				
実施例	13	90	10	—	—	40	3.42	12.3	84
	14	80	20	—	—	40	4.36	13.7	85
	15	80	20	—	—	20	5.53	12.8	88
	16	80	—	20	—	40	2.31	11.7	79
	17	70	30	—	—	20	3.01	11.8	82
比較例	9	95	5	—	—	40	1.96	2.5	40
	10	60	40	—	—	40	0.48	1.4	39
	11	80	—	—	20	40	2.00	1.5	41

＊D時間：６０℃において電流密度０．５ｍＡ／ｃｍ^{2}で充放電するとき、デンドライトが生成するため短絡する時間である。

＊＊電池性能：６０℃において電流密度０．２ｍＡ／ｃｍ^{2}で充放電するとき、１００サイクルの放電容量（初期容量を１００％として換算）

[Translation done.]